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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>B01J 23/652, 23/648, 23/62, C07C</b> <b>51/215, 57/04, 51/25</b>	<b>A1</b>	<b>(11) International Publication Number: WO 00/29106</b> <b>(43) International Publication Date: 25 May 2000 (25.05.00)</b>
<b>(21) International Application Number:</b> PCT/EP99/09038 <b>(22) International Filing Date:</b> 15 November 1999 (15.11.99)  <b>(30) Priority Data:</b> 09/193,015 16 November 1998 (16.11.98) US  <b>(71) Applicant (for all designated States except US):</b> SAUDI BASIC INDUSTRIES CORPORATION [SA/SA]; P.O. Box 5101, Riyadh 11422 (SA).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KARIM, Khalid [GB/GB]; 25 Monica Grove, Burnage, Manchester M19 2BQ (GB). BHAT, Yajnavalkya, Subrai [IN/SA]; P.O. Box 42503, Riyadh 11551 (SA). ZAHEER, Syed, Irshad [IN/SA]; P.O. Box 42503, Riyadh 11551 (SA). NAFISAH, Abdullah, Bin [SA/SA]; P.O. Box 42503, Riyadh 11551 (SA).  <b>(74) Agent:</b> SCHMITZ, Jean-Marie; Dennemeyer & Associates S.A., 55, rue des Bruyères, L-1274 Howald (LU).	<b>(81) Designated States:</b> CN, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> CATALYSTS FOR CATALYTIC OXIDATION OF PROPANE TO ACRYLIC ACID, METHODS OF MAKING AND USING THE SAME  <b>(57) Abstract</b>  A mixed metal oxide Mo-V-Ga-Pd-Nb-X (where X=La, Te, Ge, Zn, Si, In or W) catalytic system providing a higher selectivity to acrylic acid in the low temperature partial oxidation of propane with a molecular oxygen-containing gas.		

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## **TITLE OF THE INVENTION**

### **CATALYSTS FOR CATALYTIC OXIDATION OF PROPANE TO ACRYLIC ACID, METHODS OF MAKING AND USING THE SAME**

## **BACKGROUND OF THE INVENTION**

### **5   Field of Invention**

A novel mixed metal oxide catalyst for the production of acrylic acid through catalytic vapor phase partial oxidation of propane and its use for one stage selective production of acrylic acid and acrolein at lower temperatures.

### **Description of Related Art**

10       Several publications are referenced in this application. These references describe the state of the art to which this invention pertains and are hereby incorporated by reference.

The two stage vapor phase oxidation of propylene for the production of acrylic acid is known to the art. However, there is no commercial process that exists based on propane oxidation to acrylic acid. The production of acrylic acid from propane would be more  
15       attractive because of the significant price difference between propane and propylene.

There are few references reported in the literature relating to the production of acrylic acid from propane. U.S. Patent No. 5,198,580 discloses a process for partial oxidation of propane to yield acrylic acid, propylene, acrolein, acetic acid and carbon oxides by the reaction of propane in admixture with a molecular oxygen-containing gas in a reaction zone  
20       with a catalyst containing  $\text{Bi}_b\text{Mo}_c\text{V}_v\text{A}_a\text{D}_d\text{E}_e\text{O}_x$ ; where A is one or more of K, Na, Li, Cs and Tl; D is one or more of Fe, Ni, Co, Zn, Ce and La; E is one or more of W, Nb, Sb, Sn, P, Cu, Pb, B, Mg, Ca and Sr; values for a, d and e are from 0 to 10, b is from 0.1 to 10, c is from 0.1 to 20, v is from 0.1 to 10, c:b is from 2:1 to 30:1 and v:b is from 1:5 to 1 to 8. The acrylic acid yield achieved using the bismuth molybdate type of catalyst is 5.4% at 19% conversion  
25       of propane at a pressure of 20 psig and a temperature of 400°C.

European patent EP 0 608 838 A2 to Takashi et al. discloses a method of producing an unsaturated carboxylic acid, mostly in the explosive regime of the propane, air and water mixture at 380°C in the presence of a catalyst containing a mixed metal oxide of  $\text{MoVTeXO}$ , wherein X is at least one element selected from bismuth, cerium, indium, tantalum, tungsten,  
30       titanium, zirconium, chromium, manganese, iron, ruthenium, cobalt, rhodium, nickel, palladium, platinum and antimony, wherein the proportion of the respective essential components are based on the total amount of the essential components exclusive of oxygen

and satisfy the following formulae:  $0.25 < V_{Mo} < 0.98$ ,  $0.003 < V_v < 0.5$ ,  $0.003 < V_x < 0.5$ , wherein  $V_{Mo}$ ,  $V_v$ ,  $V_{Te}$  and  $V_x$  are molar fractions of Mo, V, Te and X.

Recently, Takashi et al. disclosed in another JP Patent No. 10 45 643 (98 45 643 - Feb. 1998) the formation of acrylic acid and acrolein in the presence of  $P_a Mo_b V_c W_d X_e O_n$  ( $X = Nb, Ta, Ti, Zr, Sb$ ; if  $a=1$  then  $b=1-18$ ,  $c=0-4$ ,  $d=0-4$  and  $e=0.05-20$ ) at  $380^\circ C$  achieving a yield 0.9% to acrolein and 3.5% to acrylic acid at 12% propane conversion.

The above-referenced catalysts disclosed in the literature result in low yields of acrylic acid at relatively high temperatures and produce propylene as one of the significant by-products. Propylene can be expensive to separate, especially in a recycling mode of operation.

Thus, none of the prior art discloses or suggests catalysts which provide for the selective production of acrylic acid and acrolein at low temperatures through a gas phase partial oxidation process of propane.

It would be desirable to provide a catalyst designed in such a way that a single catalyst selectively produces acrylic acid and acrolein from propane without the significant production of intermediates such as propylene.

### **OBJECTS OF THE INVENTION**

It is an object of the invention to overcome the above-identified deficiencies.

It is another object of the invention to provide an improved catalytic system for the catalytic oxidation of propane to acrylic acid.

It is a further object of the invention to provide an improved catalyst system for the single stage oxidation of propane to acrylic acid.

It is a still further object of the invention to provide methods of making and using the improved catalytic system.

The foregoing and other objects and advantages of the invention will be set forth in or be apparent from the following description.

### **SUMMARY OF THE INVENTION**

The invention relates to an improved catalyst system for the selective oxidation of propane and methods of making and using the same. According to one preferred embodiment of the invention, propane is selectively oxidized with molecular oxygen to acrylic acid and acrolein in a gas phase reaction at temperatures of  $150^\circ C$  to  $450^\circ C$  and at pressures from 1-50 bar. This is achieved using a novel catalyst with a calcined composition of  $Mo_a V_b Ga_c Pd_d Nb_e X_f$  wherein:

X= at least one element selected from the group consisting of La, Te, Ge, Zn, Si, In and W;

a is 1;

b is 0.01 to 0.9;

5 c is > 0 to 0.2;

d is 0.0000001 to 0.2;

e is > 0 to 0.2; and

f is > 0 to 0.5.

10 The numerical values of a, b, c, d, e and f represent the relative gram-atom ratios of the elements Mo, V, Ga, Pd, Nb and X, respectively, in the catalyst. The elements are preferably present in combination with oxygen in the form of various oxides.

The improved catalyst system is preferably prepared by the procedures disclosed in the examples.

15 Furthermore, this invention also relates to a selective low temperature catalytic process for the production of acrylic acid or acrolein or both by the vapor phase oxidation of propane, preferably in the non-explosive regime.

Other objects as well as aspects, features and advantages of the present invention will become apparent from a study of the present specification, including the claims and specific examples.

## 20 DESCRIPTION OF THE FIGURES

Fig. 1 is an XRD pattern of a catalyst according to one embodiment of the invention.

Fig. 2 is an XRD pattern of a comparative catalyst.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

25 One aspect of the invention relates to an improved catalytic system for the selective oxidation of propane. The catalytic system preferably comprises a calcined composition of  $\text{Mo}_a\text{V}_b\text{Ga}_c\text{Pd}_d\text{Nb}_e\text{X}_f$  wherein:

X= at least one element selected from the group consisting of La, Te, Ge, Zn, Si, In and W;

30 a is 1;

b is 0.01 to 0.9;

c is > 0 to 0.2;  
d is 0.0000001 to 0.2;  
e is > 0 to 0.2; and  
f is > 0 to 0.5.

5       According to one embodiment of the invention, the catalyst composition comprises  $\text{Mo}_a\text{V}_b\text{Ga}_c\text{Pd}_d\text{Nb}_e\text{X}_f\text{O}_y$ , wherein y is a number determined by the valence requirements of the other elements in the catalyst composition. The catalyst of the invention can be used with or without a support. Suitable supports for the catalyst include alumina, silica, titania, zirconia, zeolites, silicon carbide, Mo carbide, molecular sieves and other micro/nonporous materials,  
10   and mixtures thereof. When used with a support, the supported catalyst usually comprises from about 10 to 50% by weight of the catalyst composition, with the remainder being the support material.

Another aspect of the invention relates to methods of making the improved catalysts. The choice of the compounds used as well as the specific procedures followed in preparing a  
15   catalyst can have a significant effect on the performance of a catalyst. The elements of the catalyst composition are preferably in combination with oxygen as oxides.

Preferably, the catalyst is prepared from a solution of soluble compounds (salts, complexes or other compounds) of each of the metals. The solution is preferably an aqueous system having a pH of 1 to 10 and more preferably a pH of 1 to 7, at a temperature of from  
20   about 30 to about 100°C.

Generally, a mixture of compounds containing the elements is prepared by dissolving sufficient quantities of soluble compounds and dispersing the insoluble compounds so as to provide the desired gram-atom ratios of the elements in the catalyst composition. The catalyst composition is then prepared by removing the water and/or other solvent from the  
25   mixture of the compounds in the solution system. The dried catalyst is calcined by heating to a temperature from about 250°C to about 450°C in air or oxygen for a period of time from about one hour to about 16 hours to produce the desired catalyst composition.

Preferably, the molybdenum is introduced into the solution in the form of ammonium salts such as ammonium paramolybdate, or as organic acid salts of molybdenum such as  
30   acetates, oxalates, mandelates, and glycolates. Other partially water soluble molybdenum compounds which may be used include molybdenum oxides, molybdic acid, and chlorides of molybdenum.

Preferably, the vanadium is introduced into the solution in the form of ammonium salts such as ammonium metavanadate and ammonium decavanadate, or as organic salts of vanadium such as acetates, oxalates, and tartrates. Partially water soluble vanadium compounds such as vanadium oxides, and sulfates of vanadium can also be used. To achieve  
5 a complete solubility, a certain amount of oxalic or tartaric acid can be added.

Preferably, the gallium is introduced into the catalyst slurry in the form of salts of gallium such as oxide, chloride, nitrate, and the like.

Preferably, the palladium is introduced into the catalyst slurry in the form of Pd on activated charcoal or alumina or as a solution of salts of palladium such as acetates, chlorides,  
10 nitrates, and the like.

Preferably, the other metals are introduced into catalyst slurry in the form of salts of oxides, acetates, chlorides, nitrates, or the like.

Preferably, the niobium is used in the form of oxalates or hydrate oxides. Other sources of this metal in soluble form include compounds in which the metal is coordinated,  
15 bonded or complexed to a beta-diketonate, carboxylic acid, an amine, an alcohol, or an alkanolamine.

According to one preferred embodiment, the catalyst is prepared by the following general procedure. Aqueous solutions of vanadium and molybdenum are prepared separately. The vanadium solution is mixed with the molybdenum solution at a specified  
20 temperature and pH. The remaining required components are slowly added to the combined gel solution. After mixing, the resultant gel is dried to incipient wetness with continuous stirring.

After drying the resultant gel mixture at 120°C for 16 hours, the resultant catalyst is heated to about 350°C at a rate of 2°C per minute and calcined at this temperature in air for 4  
25 hours to produce the desired oxide composition.

Another aspect of the invention relates to a method of using the inventive catalyst system for the selective oxidation of propane to the acrylic acid.

The raw material used as the source of the propane can be a gas stream which contains at least three volume percent of propane or a mixture of propylene/propane. The gas  
30 stream can also contain some amounts of the C<sub>2</sub> or C<sub>4</sub> alkane and alkenes, preferably less than thirty volume percent of each. The gas stream can also contain major amounts, more than five volume percent, of diluents such as nitrogen/argon, carbon dioxide, and water in the form of steam.

In carrying out the process, the reaction mixture generally contains one mole of propane, 0.01 to 2.0 moles of molecular oxygen either as pure oxygen or in the form of air, and zero to 4.0 moles of water in the form of steam.

5 Molecular oxygen sources for the feed include purified oxygen, air and oxygen-enriched air, depending on the economics of separation and the hydrocarbon conversion achieved. The ratio of propane to oxygen varies with the desired conversion and the selectivity of the catalyst, but generally is in the range of 1/5-5/1.

10 The oxygen concentration in the feed gas mixture can vary widely, from 0.1 to 50% or higher of the feed mixture by applying proper measures to avoid explosion problems. Air is the preferred source of oxygen in the feed. The amount of oxygen present may be a stoichiometric amount, or lower, of the hydrocarbons in the feed.

The reaction can also be affected especially in the presence of diluents such as argon, nitrogen or steam. The ratio of propane to diluents can be in the range of 1/5-1/1.

15 The water vapor or steam may be used as a reaction diluent and as a heat moderator for the reaction. It also can act as a desorption accelerator of the reaction product in the vapor phase oxidation reaction. Other gases may be used as reaction diluents or heat moderators such as helium, nitrogen and carbon dioxide.

The liquid products of the reaction can be separated from the unreacted feed hydrocarbons by condensation or scrubbing, usually by water or dilute acid.

20 The gaseous components of the reaction mixture preferably include propane, oxygen or oxygen and diluents, and these components are preferably uniformly admixed prior to being introduced into the reaction zone. The components may be preheated, individually or after being admixed, prior to being introduced into the reaction zone which should have a temperature of from about 150°C to about 450°C.

25 The reaction zone generally has a pressure of from 1 to 50 bar, preferably from 1 to 30 bar; a temperature of from about 150°C to about 450°C, preferably from 200 to 300°C; a contact time between the reaction mixture and the catalyst of from about 0.01 second to 100 seconds, preferably from 0.1 second to 10 seconds; and a space hourly velocity of from about 50 to about 50,000 h<sup>-1</sup>, preferably from 100 to 10,000 h<sup>-1</sup> and most preferably from 200 to 30,000 h<sup>-1</sup>.

The contact time is defined as the ratio between the apparent volume of the catalyst bed and the volume of the gaseous reaction mixture feed to the catalyst bed under the given reaction conditions in a unit of time.



The space velocity is calculated by determining the total reactor outlet gas equivalent in liters of the total effluent evolved over a period of one hour divided by the liters of catalyst in the reactor. This room temperature volume is converted to the volume at 0°C at 1 bar.

The reaction pressure may be initially provided by the feed of the gaseous reactant  
5 and diluent and after the reaction has commenced, may be maintained by the use of a suitable back-pressure controller placed on the reactor outlet stream.

The reaction temperature is provided by placing the catalyst bed within a tubular converter having walls placed in a furnace heated to the desired reaction temperature.

One surprising advantage of the catalyst systems of the invention is the higher yields  
10 of acrylic acid achieved. Preferably, the oxidation can provide at least a 30% yield of acrylic acid.

The oxidation performed according to the invention preferably provides a selectivity to acrylic acid of at least 50% per single pass through the reaction zone, more preferably at least 70%.

15 Preferably, less than 1% propylene is formed using the catalyst system. More preferably, no detectable propylene is formed as a by-product.

The process is generally carried out in a single stage with all the oxygen and reactants being supplied as a single feed with non-reacted initial reactants being recycled. However, multiple stage addition of oxygen or hydrocarbon to the reactor can be used and/or recycling  
20 of un-reacted gases with purge mode can be applied to improve the overall productivity and/or yield of the desired products.

The methods of using the catalyst of the invention are not limited to the oxidation of propane to acrylic acid and acrolein. The catalyst may also be used for oxidizing n/iso C4, C5 in the vapor phase with molecular oxygen to produce the corresponding alpha-beta  
25 unsaturated carboxylic acids.

### **EXAMPLES**

The following examples are illustrative of some of the products and methods of making the same falling within the scope of the present invention. They are, of course, not to be considered in any way limitative of the invention. Numerous changes and modifications  
30 can be made with respect to the invention.

The catalyst samples prepared in the examples were evaluated by using the following method.

**Catalyst Testing:**

Catalyst evaluations were carried out in a stainless steel fixed bed tubular reactor under standard process conditions. The gas feed compositions used for the evaluation of the catalysts contained propane, oxygen and nitrogen. Reactions were carried out at a  
5 temperature of 300°C, pressure of 15 psig and at space velocity of about 1,090 h<sup>-1</sup>.

Reaction products were analyzed on-line by gas chromatography. Oxygen, argon and carbon monoxide were analyzed using a 2.5 m by 3 mm column of 13X molecular sieve. Carbon dioxide, propane and propylene were analyzed using a 2 m by 3mm column packed with material sold under the trade name HAYESEP Q®. Liquids products (acrylic acid,  
10 acrolein, acetic acid and water) were collected for a certain period in the cold trap and were analyzed using a 2 m by 3 mm column packed with material sold under the trademark PORAPAK Q®. In all cases, the conversion and selectivity calculations were based on the reaction stoichiometry.

**EXAMPLE 1:** [Mo<sub>1</sub>V<sub>0.398</sub>Ga<sub>1.0E-05</sub>Pd<sub>1.90E-04</sub>Nb<sub>0.125</sub>Te<sub>0.23</sub>]

15 Ammonium metavanadate (Aldrich Chemicals, Assay = 99.0%) in the amount of 7.6 grams was added to 80 ml of distilled water and heated to 90°C with stirring. 3.4 grams of niobium oxide (80% Nb<sub>2</sub>O<sub>5</sub>), 28 grams of oxalic acid, and 28.8g ammonium paramolybdate tetra hydrated (Aldrich Chemicals A.C.S.-12054-85-2) were added to the vanadate solution to make a gel mixture. The required amount of palladium followed by telluric acid and gallium  
20 oxide were added slowly to gel mixture. The gel mixture was stirred vigorously to achieve a homogeneous gel mixture which was then dried slowly to incipient dryness with continuous stirring.

The resulting solid was put in a China dish and dried additionally in an oven at 120 °C. The dried material was cooled to room temperature and placed in a furnace where the  
25 catalyst is calcined at 350°C for 4 to 16 hours. The temperature was raised from room temperature to 350°C at the rate of 2°/min and thereafter held at 350 °C for four hours.

The calcined catalyst was formulated into uniform particles of the 40-60 mesh size and evaluated for the propane oxidation reaction. The catalyst was evaluated at a temperature of 300 °C using a feed mixture containing propane:oxygen:nitrogen (20:10:70). The reaction  
30 product showed the following results:

Propane Conversion (%)	:	26.45
Acrylic acid sel. (%)	:	31
Acrolein sel. (%)	:	1

Acetic acid sel. (%)	:	21
CO <sub>x</sub> sel. (%)	:	47

The overall reaction products showed 53 % oxygenated product and 47 % total oxidation product.

5 **EXAMPLE 2:** [Mo<sub>1</sub>V<sub>0.398</sub>Ga<sub>1.0E-05</sub>Pd<sub>1.90E-04</sub>Nb<sub>0.125</sub>Te<sub>0.23</sub>La<sub>1.0E-05</sub>]

The procedure was the same as Example 1 except the required amount of lanthanum nitrate was also added in the last step of preparation.

The calcined catalyst was formulated into uniform particles of the 40-60 mesh size and evaluated for the propane oxidation reaction. The catalyst was evaluated at a temperature  
10 of 300°C using a feed mixture containing propane: oxygen: nitrogen (20:10:70). The reaction product showed the following results:

Propane Conversion (%)	:	21.21
Acrylic acid sel. (%)	:	21
Acrolein sel. (%)	:	1
15 Acetic acid sel. (%)	:	13
CO <sub>x</sub> sel. (%)	:	65

The overall reaction products showed 35% oxygenated product and 65% total oxidation product.

**EXAMPLE 3:** [Mo<sub>1</sub>V<sub>0.398</sub>Ga<sub>1.0E-05</sub>Pd<sub>1.90E-04</sub>Nb<sub>0.125</sub>Te<sub>0.23</sub>Zn<sub>1.0E-05</sub>]

20 A catalyst was prepared with the procedure of Example 1 with the addition of lanthanum nitrate. The catalyst was evaluated at 320°C using feed mixture containing propane and oxygen (80:20). The reaction product showed 65% selectivity to acrylic acid, 10% acetic acid, 5% to propylene and 20% to CO<sub>x</sub> products at 10.4% propane conversion. Overall reaction product showed about 75% selectivity to oxygenated value added products.

25 **EXAMPLE 4:** [Mo<sub>1</sub>V<sub>0.398</sub>Ga<sub>1.0E-05</sub>Pd<sub>1.90E-04</sub>Nb<sub>0.125</sub>Te<sub>0.23</sub>Zn<sub>1.0E-05</sub>]

The procedure was same as described in Example 1 except the required amounts of zinc nitrate and telluric acid were also added in the last step of preparation. The calcined catalyst was formulated into uniform particles of the 40-60 mesh size and evaluated for the propane oxidation reaction. The catalyst was evaluated at a temperature of 300°C using a  
30 feed mixture containing propane: oxygen: nitrogen (20:10:70). The reaction product showed the following results:

Propane Conversion (%)	:	20
Oxygen Conversion (%)	:	100

Acrylic acid sel. (%)	:	26
Acrolein sel. (%)	:	1
Acetic acid sel. (%)	:	15
CO <sub>x</sub> sel. (%)	:	58

- 5 The overall reaction products showed 42% oxygenated product and 58% total oxidation product.

**EXAMPLE 5:** [Mo<sub>1</sub>V<sub>0.398</sub>Ga<sub>1.0E-05</sub>Pd<sub>1.90E-04</sub>Nb<sub>0.125</sub>Te<sub>0.23</sub>]

- The catalyst is same as described in Example 1. The calcined catalyst was formulated into uniform particles of the 40-60 mesh size and was evaluated at a temperature of 300°C using a feed mixture containing propane:oxygen (95.25:4.75). The reaction product showed the following results:

Propane Conversion (%)	:	4.22
Oxygen Conversion (%)	:	100
Acrylic acid sel. (%)	:	45.5
15 Acrolein sel. (%)	:	5.5
Acetic acid sel. (%)	:	12
CO <sub>x</sub> sel. (%)	:	37

The overall reaction products showed 63% oxygenated product and 37% total oxidation product.

20 **EXAMPLE 6:** [Mo<sub>1</sub>V<sub>0.398</sub>Ga<sub>1.0E-05</sub>Pd<sub>1.90E-04</sub>Nb<sub>0.125</sub>Te<sub>0.23</sub>]

The catalyst used for this example is same as in Example 1. The calcined catalyst was formulated into uniform particles of the 40-60 mesh size and evaluated for the propane oxidation reaction. The catalyst was evaluated at a temperature of 300°C using a feed mixture containing propane:oxygen (90:10).

- 25 The reaction products showed with following results:

Propane Conversion (%)	:	9
Oxygen Conversion (%)	:	100
Acrylic acid sel. (%)	:	35.5
Acrolein sel. (%)	:	3.5
30 Acetic acid sel. (%)	:	10
CO <sub>x</sub> sel. (%)	:	51

The overall reaction products showed 49% oxygenated product and 51% total oxidation product.

**EXAMPLE 7:**  $[\text{Mo}_1\text{V}_{0.398}\text{Ga}_{1.0\text{E}-05}\text{Pd}_{1.15\text{E}-04}\text{Nb}_{0.125}\text{Te}_{0.30}]$ 

The procedure for the preparation of the catalyst is same as described in Example 1 except different amounts Pd and tellurium were added. The calcined catalyst was formulated into uniform particles of the 40-60 mesh size and evaluated for the propane oxidation reaction. The catalyst was evaluated at a temperature of 300°C using a feed mixture containing propane:oxygen:nitrogen (20:10:70). The reaction products showed the following results:

	Propane Conversion (%)	:	17.14
	Oxygen Conversion (%)	:	100
10	Acrylic acid sel. (%)	:	13
	Acrolein sel. (%)	:	1
	Acetic acid sel. (%)	:	10
	CO <sub>x</sub> sel. (%)	:	76

The overall reaction products showed 24% oxygenated product and 76% total oxidation product.

The BET surface area for the catalysts described in above Examples 1-6 varied from 20 to 35 m<sup>2</sup>/g.

An XRD pattern for a catalyst according to one embodiment of the invention is shown in Figure 1. The catalysts disclosed in the present invention preferably have a structure which produces diffused or poorly crystallized patterns with a strong reflection peak at 22 (4.00 angstroms) and a very broad peak at 27 (3.57 angstroms) two theta values. Generally, to obtain this structure, a catalyst has to be prepared by the methods described above. The very broad peak at 3.57 angstroms is a kind of diffused peak and is difficult to attribute to any one phase. However, when these types of catalysts are calcined at higher temperature other well defined reflections appear and these are not active for the activation of alkanes to oxygenates product, as shown in Example No. 8 (below).

The catalysts of the present invention showed an optimum redox behavior resulting a high activity and highly selective towards the partial oxidation products. Based on catalytic data, the following general characteristics can be concluded for the catalysts disclosed in the present application.

1. The catalysts show high selectivity to acrylic acid at low temperature.
2. The oxidation of propane shows lower • T of 10-15°C. Lower • T can have a positive impact on the reactor design.

3. Relative selectivity to oxygenated products (acrylic acid, acrolein and acetic acid) depends on the catalyst composition, reaction temperature, space velocity, pressure and feed composition (alkane, oxygen, steam, nitrogen).

**Comparative EXAMPLE 8:**  $[\text{Mo}_1\text{V}_{0.39}\text{Nb}_{0.125}\text{Te}_{0.23}]$

5       The catalyst composition and procedure is same as described in EP patent publication No. 0 608 838 for comparative purposes. The catalyst was calcined at 600°C as described in the EP patent publication. The XRD pattern of the catalyst, Figure 2, shows all well defined reflections at 22.1, 28.2, 36.2, 45.2 and 50 at two theta values, as described in the EP patent publication. The calcined catalyst was formulated into uniform particles of the 40-60 mesh  
10 size and evaluated for the propane oxidation reaction at temperatures of 300 and 380°C with a feed mixture containing propane: oxygen: nitrogen (20:10:70). The catalyst was not active at both temperatures.

      The above description of the invention is intended to be illustrative and not limiting. Various changes or modifications in the embodiments described may occur to those skilled in  
15 the art. These can be made without departing from the spirit or scope of the invention.

**Claims:**

1. A catalyst for selective oxidation of propane to oxygenated products including acrylic acid, acrolein and acetic acid, said catalyst system containing a catalyst composition comprising  $\text{Mo}_a\text{V}_b\text{Ga}_c\text{Pd}_d\text{Nb}_e\text{X}_f$

5 wherein:

X = at least one element selected from La, Te, Ge, Zn, Si, In and W;

a is 1;

b is 0.01 to 0.9;

c is > 0 to 0.2;

10 d is 0.0000001 to 0.2;

e is > 0 to 0.2;

f is > 0 to 0.5; and

wherein the numerical values of a, b, c, d, e and f represent the relative gram-atom ratios of the elements Mo, V, Ga, Pd, Nb and X, respectively, in the catalyst and the elements  
15 are present in combination with oxygen.

2. A catalyst for selective oxidation of propane to oxygenated products including acrylic acid, acrolein and acetic acid made by process comprising the steps of:

(a) combining the elements Mo, V, Ga, Pd, Nb and X to form a mixture in the following ratio:  $\text{Mo}_a\text{V}_b\text{Ga}_c\text{Pd}_d\text{Nb}_e\text{X}_f$ , wherein:

20 X = at least one element selected from La, Te, Ge, Zn, Si, In and W;

a is 1;

b is 0.01 to 0.9;

c is > 0 to 0.2;

d is 0.0000001 to 0.2;

25 e is > 0 to 0.2; and

f is > 0 to 0.5; and

b) calcining said mixture to form said catalyst.

3. The catalyst according to claim 1, wherein the catalyst composition exhibits two X-rays diffraction peaks at the following two theta values: a strong peak at 22 (+0.3) and  
30 a very broad peak at 27 (+0.5).

4. The catalyst of claim 1, wherein said catalyst is a supported catalyst comprising a support.

5. The catalyst of claim 2, wherein said catalyst is a supported catalyst comprising a support.

6. The catalyst of claim 4, wherein said support comprises alumina, silica, titania, zirconia, silicon carbide, Mo-carbide, zeolites, molecular sieves or other microporous/nanoporous materials.

7. The catalyst of claim 4, wherein said supported catalyst comprises from 0 to 50% by weight catalyst composition and 50 to 95% by weight support.

8. A single stage catalytic process for direct conversion of propane to acrylic acid and acrolein by means of propane oxidation comprising oxidizing propane in a reaction mixture comprising (i) propane or propane/propylene and (ii) oxygen or a compound capable of providing oxygen in a reaction zone in the presence of the catalyst of claim 1.

9. The process according to claim 8, wherein the reaction mixture further comprises C2-C8 alkane.

10. The process according to claim 9, wherein the alkane is ethane, propane, isobutane, n-butane or mixtures thereof.

11. The process of claim 8, wherein said catalyst is in the form of a fixed bed and said oxidation is carried out by a feed mixture comprising propane fed into the reaction zone.

12. The process of claim 8, wherein said catalyst is in the form of a fluidized bed and said oxidation is carried out by a feed mixture comprising propane fed into the reaction zone.

13. The process of claim 12, wherein said feed mixture further comprises air.

14. The process of claim 12, wherein said feed mixture comprises oxygen.

15. The process of claim 12, wherein said feed mixture comprises molecular oxygen ranging from 0.1 to 50% by volume of the feed.

16. The process of claim 12, wherein said feed mixture is diluted with steam in an amount ranging from 0 to 60% by volume.

17. The process of claim 11, wherein oxidation is achieved while operating in gas phase at a temperature of from 100 to 450°C, under a pressure of from 1 to 50 bars, and with a contact time between reaction mixture and the catalyst of from 0.1 to 10 seconds.

18. The process of claim 1, wherein said oxidation provides 80% selectivity to oxygenated products (acrylic acid, acrolein and acetic acid).



19. The process of claim 11, wherein said oxidation of propane produces no detectable propylene as a by-product using molecular oxygen ranging from 0.1 to 50% of the feed.

20. The process of claim 11, further comprising multi-step introduction of oxygen into the feed mixture to increase the yield, selectivity or both yield and selectivity of desired products.

21. A process for performing a catalytic chemical reaction in fluid phase comprising contacting at least one reactant in fluid phase under suitable reaction conditions with catalyst containing a catalyst composition comprising  $\text{Mo}_a\text{V}_b\text{Ga}_c\text{Pd}_d\text{Nb}_e\text{X}_f$ ,  
10 wherein: X = at least one element selected from La, Te, Ge, Zn, Si, In and W;  
a is 1;  
b is 0.01 to 0.9;  
c is > 0 to 0.2;  
d is 0.0000001 to 0.2;  
15 e is > 0 to 0.2; and  
f is > 0 to 0.5.

22. A process for performing a catalytic chemical reaction comprising the step of introducing a reactant in fluid phase into a reaction zone containing a catalyst having a catalyst composition made by a method comprising the steps of:

20 a) combining the elements Mo, V, Ga, Pd, Nb, and X to form a mixture in the following ratio:  $\text{Mo}_a\text{V}_b\text{Ga}_c\text{Pd}_d\text{Nb}_e\text{X}_f$ ,

wherein: X = at least one element selected from La, Te, Ge, Zn, Si, In and W;

a is 1;  
b is 0.01 to 0.9;  
25 c is > 0 to 0.2;  
d is 0.0000001 to 0.2;  
e is > 0 to 0.2; and  
f is > 0 to 0.5; and

(b) calcining said mixture.

30 23. The process of claim 22, wherein said catalytic chemical reaction converts one or more fluid phase reactants to one or more fluid phase products.

24. The process of claim 22, wherein said catalytic chemical reaction oxidizes  $\text{C}_2$ - $\text{C}_8$  alkanes or alkenes to corresponding acids.

25. The process of claim 23, wherein said one or more fluid phase reactants comprise propane and said one or more fluid phase products comprise acrylic acid.

26. The process of claim 23, wherein said one or more fluid phase reactants comprise alpha-beta unsaturated aliphatic aldehydes and oxygen and said one or more fluid  
5 phase products comprise alpha-beta unsaturated carboxylic acids.

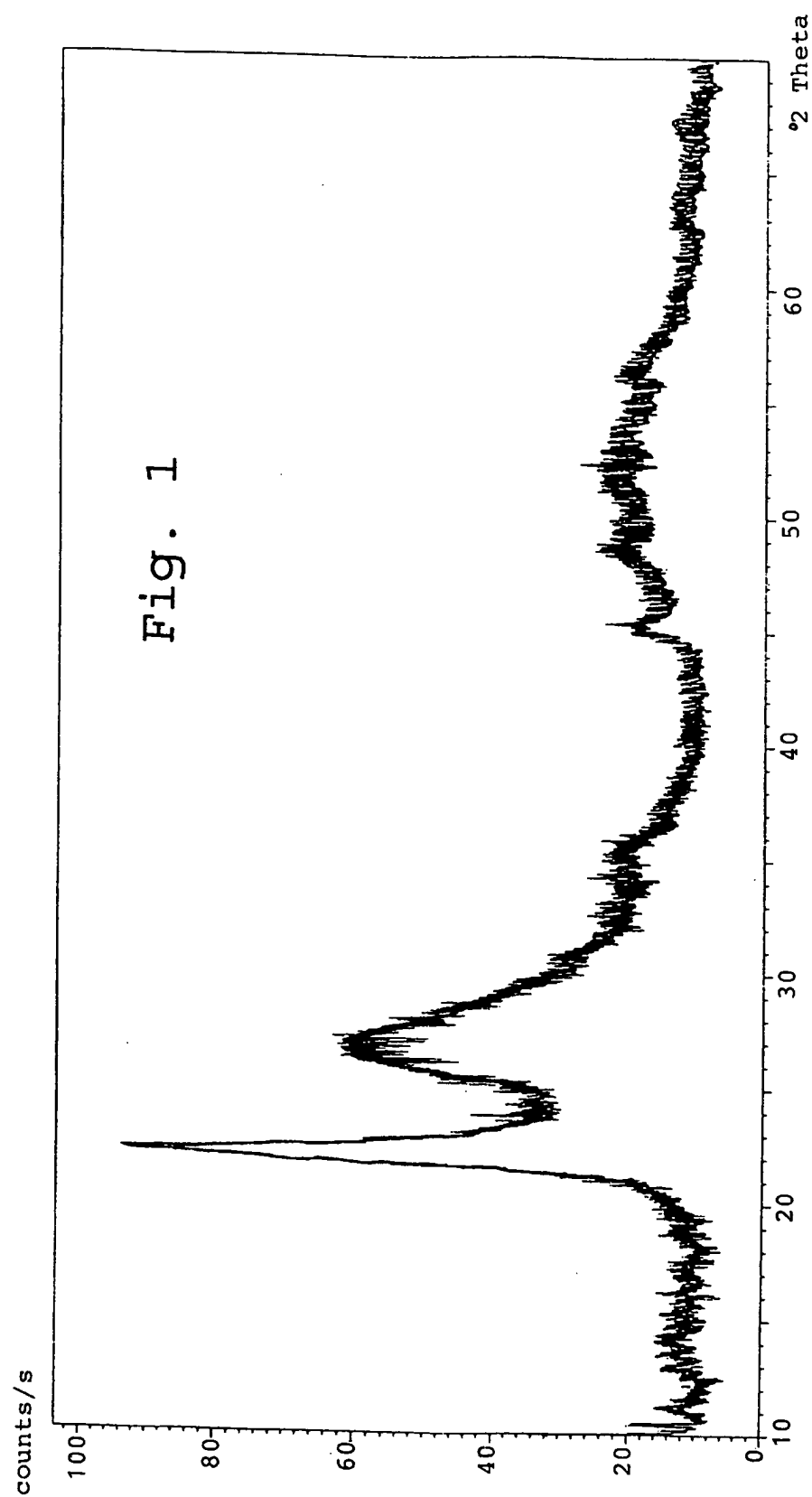
27. A process of forming the catalyst of claim 1, comprising the steps of:

- a) forming a mixture containing Mo, V, Ga, Pd, Nb, and X in solution;
- b) drying said mixture to form a dried solid material; and
- c) calcining said dried solid material to form said catalyst.

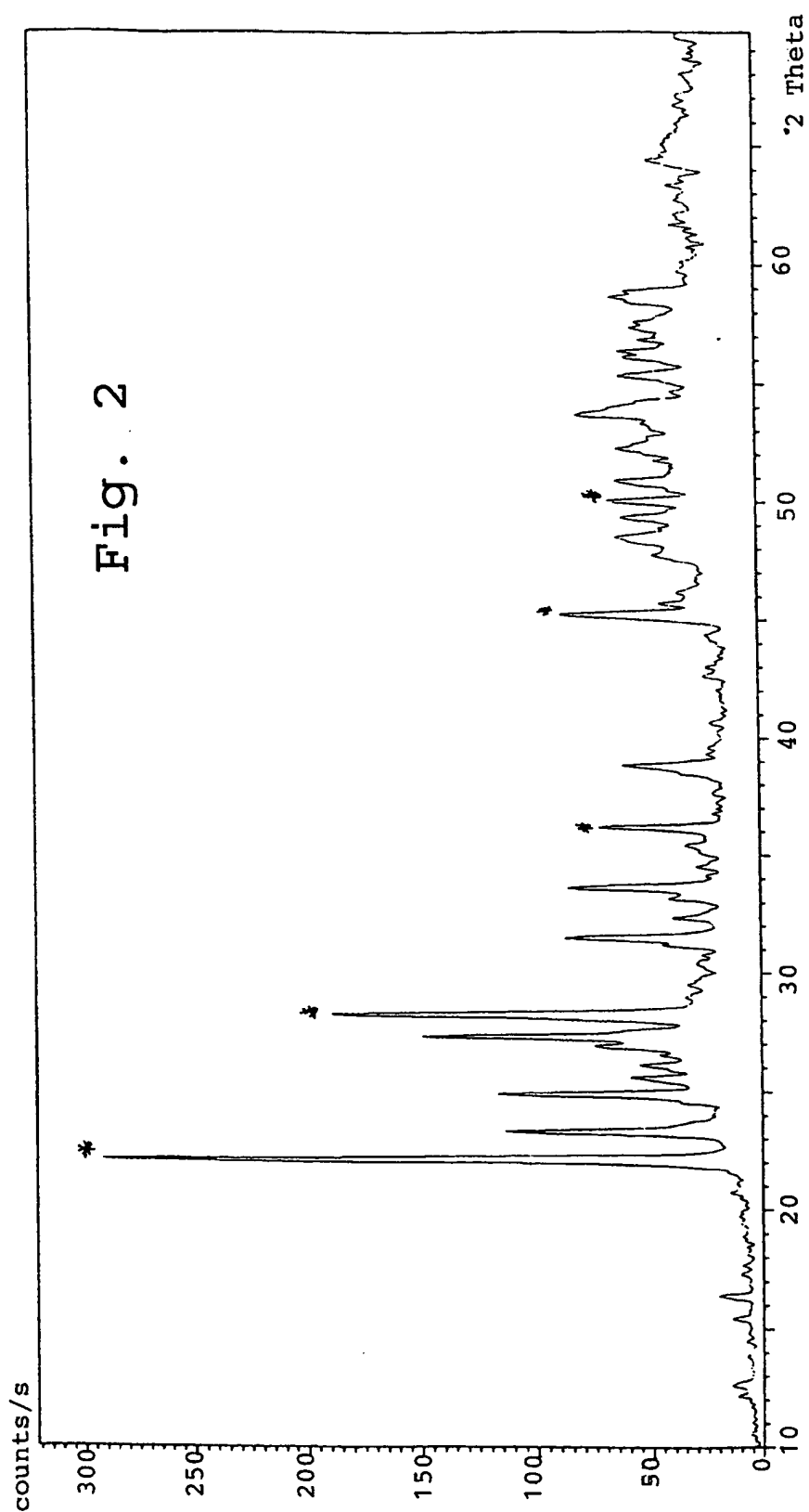
10 28. The process of claim 27, wherein said calcining comprises heating said dried solid material to a calcining temperature from about 250 to 450°C in air or oxygen for period of time from about one hour to about 16 hours.

29. The process of claim 8, wherein said catalyst is in the form of a solid moving bed and said oxidation is carried out by a feed comprising propane or propane/propylene fed  
15 into the reaction zone.

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# INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/EP 99/09038

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/652 B01J23/648 B01J23/62 C07C51/215 C07C57/04  
C07C51/25

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	DE 197 45 902 A (HOECHST AG) 22 April 1999 (1999-04-22) claims 1,8 page 3, line 56 - line 61	1,2,4-6, 21
Y		8-18, 22-29
X	DE 197 17 076 A (HOECHST AG) 29 October 1998 (1998-10-29) claims 1,10	1,2,4-6, 21
X	DE 196 30 832 A (HOECHST AG) 5 February 1998 (1998-02-05) claims 1,7	1,2,4-6, 21
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

8 March 2000

Date of mailing of the international search report

16/03/2000

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/09038

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI  Section Ch, Week 199813  Derwent Publications Ltd., London, GB;  Class E17, AN 1998-140953  XP002132109  &amp; JP 10 017523 A (MITSUBISHI CHEM CORP),  20 January 1998 (1998-01-20)  abstract</p>	
Y	<p>EP 0 608 838 A (MITSUBISHI CHEM IND)  3 August 1994 (1994-08-03)  cited in the application  claim 1; example 4</p>	<p>8-18,  22-29</p>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter: International Application No

PCT/EP 99/09038

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19745902 A	22-04-1999	WO 9920592 A	29-04-1999
DE 19717076 A	29-10-1998	WO 9847850 A	29-10-1998
		EP 0979222 A	16-02-2000
		NO 995085 A	18-10-1999
DE 19630832 A	05-02-1998	AU 4010597 A	25-02-1998
		BG 103119 A	29-10-1999
		CN 1231656 A	13-10-1999
		CZ 9900316 A	14-07-1999
		WO 9805619 A	12-02-1998
		EP 0915821 A	19-05-1999
		NO 990363 A	26-01-1999
		PL 331374 A	05-07-1999
		SI 9720051 A	31-10-1999
JP 10017523 A	20-01-1998	NONE	
EP 0608838 A	03-08-1994	JP 7010801 A	13-01-1995
		JP 6279351 A	04-10-1994
		DE 69402567 D	22-05-1997
		DE 69402567 T	27-11-1994
		US 5380933 A	10-01-1995